Quantitative Analysis of Reinforcing Particles in Polyurethanes by STXM

A.P. Hitchcock[1], I. Koprinarov[1], T. Tyliszczak[1], S.G. Urquhart[2], A.P. Smith[2], H.W. Ade[2], E.G. Rightor[3], W. Lidy[3], M.T. Dineen[3], G.E. Mitchell[3], W.S. Steele[4], G. Meigs[4], T. Warwick[4]

1. BIMR, McMaster University, Hamilton, L8S 4M1 Canada
2. North Carolina State University, Raleigh, NC 27695 USA
3. Dow Chemical, Midland, MI 48667 USA
4. Advanced Light Source, Berkeley Lab, Berkeley, CA 94720 USA

INTRODUCTION

Polyurethane polymers are widely used in the automotive and furnishings industries. Several different strategies are used to make foams with higher hardness [1]. Copolymer polyol particles (CPP) which are polymer dispersions in polyether polyol, inorganic fibers, and low molecular weight cross-linker polyols are preferred for stiffening slabstock foams. In order to understand how reinforcing particles like co-polymer polyols affect mechanical properties such as elastic modulus, tear strength and resiliency, and in order to develop improved CPP substances, it is important to have analytical techniques which can probe the morphology and chemistry at the required spatial scale. Scanning transmission X-ray microscopy (STXM, BL 7.0) has been used to study the morphology, size distributions, spatial distributions, and quantitative chemical compositions of co-polymer polyol reinforcing particles in a polyurethane [2]. Images at selected photon energies in the C 1s, N 1s and O1s regions allow unambiguous identification of CPP type down to particle sizes of ~50 nm. This work exemplifies only one of many unique opportunities STXM provides for chemical micro-analysis of materials of industrial relevance.

EXPERIMENTAL AND DATA ANALYSIS PROCEDURES

A toluene diisocyanate-based (TDI) polyurethane containing two types of copolymer polyol (CPP) reinforcing particles was studied. One CPP is poly(styrene-*co*-acrylonitrile) (SAN), the other is an aromatic-carbamate rich poly-isocyanate poly-addition product (PIPA™), derived from methylene diisocyanate (MDI). Thin sections were prepared by cryo-microtoming compressed molded blocks of slabstock polyurethane at -120^{o}C using a Reichert-Jung FC4E microtome. ~100 nm thick sections were transferred dry to uncoated copper grids. Images, and image sequences were recorded with the BL 7.0 STXM, using ~100 meV energy resolution and ~100 nm spatial resolution. Shuttering, rapid scanning (typical dwells of 0.1-0.2 ms/pixel) and optimal energy sampling were used to minimize radiation dose. Although there was some mass loss (10-30%) in the poyether rich matrix regions after image sequence acquisition, the critical analytical near edge features were recorded prior to any significant damage. Typically, sequences consisting of images at 100 energies, each 150x150 pixels, 15x15 μm (100 nm pixels), 0.2 ms/pixel dwell, are recorded with an overall acquisition time of ~15 minutes of which ~10 minutes involved beam on the sample.

Image sequences were analyzed with AXIS [3], a general purpose IDL widget which implements routines originally developed by Chris Jacobsen and Carl Zimba [4]. After alignment and conversion to optical density, quantitative compositional maps were generated from the 3d data volume by singular value decomposition or pixel-by-pixel cuurve fits, in both cases using reference spectra of the components placed on a mass thickness scale by matching to Henke [5] atomic mass coefficient curves for the known compositions.

RESULTS AND DISCUSSION

Figure 1 compares transmission electron microscopy (TEM, JEOL 2000FX) and STXM images in the C 1s, N 1s and O 1s regime. The CPP particles are high contrast but chemically

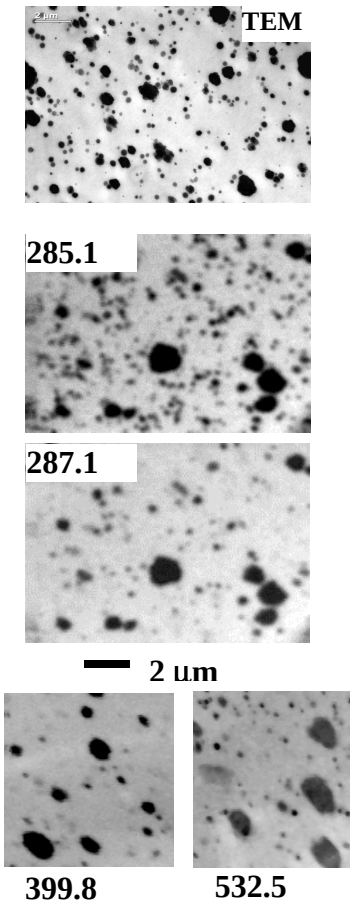

Fig. 1 Comparison of TEM, C 1s, N 1s and O 1s STXM images of SAN. The two C 1s images are of the same area.

indistinguishable by TEM. Differences in the NEXAFS spectra of the PIPA, SAN CPP particles and the matrix provide a basis for identification with STXM (**Figure 2)** which plots C 1s, N 1s and O 1s NEXAFS reference spectra derived from image sequences. The strong $\pi^*_{C\equiv N}$ resonances at 286.7 eV (C1s) and 399.8 eV (N1s) provide excellent identification of the SAN particles, whereas the strong ring $\pi^*_{C=C}$ resonance at 285.1 eV highlights both types of CPP relative to the matrix. The O 1s image at the $\pi^*_{C=O}$ resonance at 532.5 eV highlights the PIPA, but less than might be hoped for since the SAN particles actually contain some polyether oxygen, have density contrast relative to the matrix, and since the O 1s absorption signal rides on a large C 1s and N 1s background.

The difference of the 285.1 and 287.1 eV images shown in Fig. 1 could be used to isolate the PIPA particles [2]. Alternatively, pixel-by-pixel curve fit analysis of full image sequences provides a powerful means of generating component maps of each CPP. **Figure 3** presents composition maps extracted from a C 1s image sequence. In addition to isolating the two types of CPP particles we have extracted the styrene and acrylonitrile components separately in order to examine the degree of uniformity of the composition of the SAN polymer blend particles. Detailed analysis of multiple SAN particles indicates that the blend composition is constant within statistical precision and in good agreement with that from the synthetic formulation [2]. Composition maps from N 1s and O 1s image sequences are of lower quality than C 1s, but certainly adequate to identify and provide semi-quantitative maps of each component [2].

These results demonstrate that STXM microscopy can provide quantitative chemical analysis on submicron regions of quite radiation sensitive polymers with better than 5% relative precision. Other examples of quantitative STXM include analysis of urea and urethane compositions in polyurethanes [6,7], PS, Br-PS thin film structures [8], and polystyrene/poly(methyl

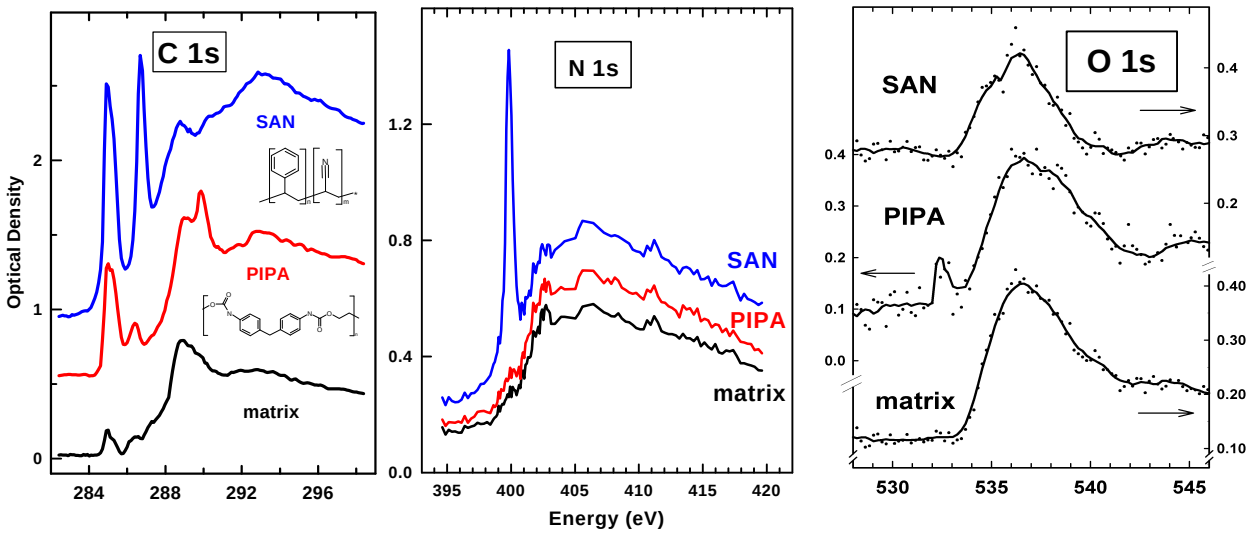

Figure 2 C 1s, N 1s and O 1s NEXAFS of the SAN, PIPA CPPs and the TDI polyurethane matrix.

methacrylate) blends [9]. The precision demonstrated in this work should be achievable whenever there are characteristic spectral signatures of the individual components and when the radiation damage rates are low enough to allow acquisition of representative images and spectra. Particle analysis shows the mean PIPA particle size is about 150 nm diameter and about a third of the particles are below 100 nm in size [2]. With careful image alignment it is possible to obtain quantitative analysis of features at the limits of spatial resolution. Currently this is about~100 nm on the present BL 7.0 STXM. An upgrade to be installed in 2000 will achieve spatial resolution at the diffraction limit of the zone plates (~50 nm).

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Principal investigators:
Adam Hitchcock, BIMR, McMaster University. email: aph@mcmaster.ca. Ph: 905 525-9140.
Ed Rightor, Dow Analytical. email: egrightor@dow.com Ph: 517 636-0221

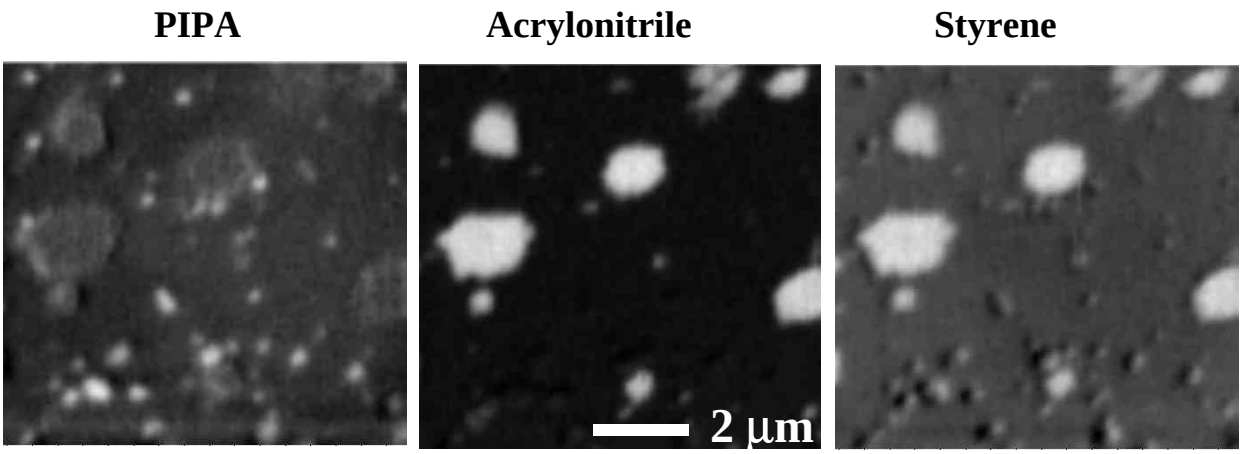

Figure 3 Component maps of the PIPA and styrene/acrylonitrile co-polymer polyol particles derived from pixel-by-pixel analysis of a C 1s image sequence.